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A process for purifying yttrium metal

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A process for purifying yttrium metal

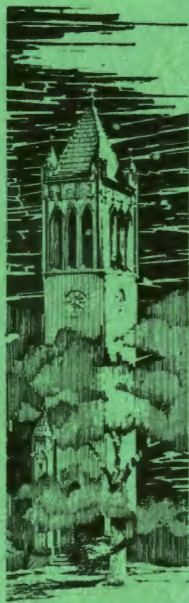
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Disciplines

Metallurgy

IS-984



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YTTRIUM METAL**

by

**O. N. Carlson, J. A. Haeffling
and F. A. Schmidt**

AMES LABORATORY

**RESEARCH AND
DEVELOPMENT
REPORT**

U.S.A.E.C.



PHYSICAL SCIENCES READING ROOM

IS-984

Metals, Ceramics and Materials (UC-25)
TID-4500, September 1, 1964

UNITED STATES ATOMIC ENERGY COMMISSION

Research and Development Report

A PROCESS FOR PURIFYING
YTTRIUM METAL

by

O. N. Carlson, J. A. Haefling
and F. A. Schmidt

September, 1964

Ames Laboratory

at

Iowa State University of Science and Technology
F. H. Spedding, Director
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CONTENTS

ABSTRACT.....	5
INTRODUCTION.....	5
EXPERIMENTAL PROCEDURE AND RESULTS	6
Materials	6
Preparation and Purification of YCl_3 and Magnesium	7
Preparation of Y-29 wt% Mg Alloy	9
Preparation of Yttrium Metal	10
Other Procedures Used for Metal Refinement	13
SUMMARY	14
ACKNOWLEDGMENT	15
REFERENCES	16

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A PROCESS FOR PURIFYING YTTRIUM METAL

O. N. CARLSON, J. A. Haefling, and F. A. Schmidt

ABSTRACT

A process is described for purifying crude or scrap yttrium metal by first reacting the yttrium with fused MgCl_2 and then purifying the magnesium and YCl_3 products by co-distillation. Dissolution and purification are carried out in a single heating step. The purified YCl_3 is reduced with calcium in the presence of the magnesium to form a Y-Mg intermediate alloy which is processed to yttrium sponge. Further refinement of the metal was obtained employing a salt extraction step and electron beam melting. Yttrium of 99.9+% purity was obtained from metal of 99.3% purity.

INTRODUCTION

In 1957 and 1958 a considerable quantity of yttrium metal was produced for the U.S. Atomic Energy Commission at the Ames Laboratory. The metal was prepared by the reduction of YF_3 with calcium or lithium to form a low melting Y-Mg intermediate alloy. This alloy was then converted to yttrium sponge which was consolidated into ingot form.¹ The yttrium metal prepared in this manner was of 99.3 wt% purity and exhibited a limited amount of ductility at room temperature.

The purpose of this investigation was to develop a metallurgical process whereby metal of this quality could be conveniently upgraded to a high purity material. Habermann and Daane² successfully purified yttrium in small quantities by vacuum distillation. Other refining methods such as vacuum melting, zone refining, and solid state electrolysis have been found to only partially purify crude yttrium metal.³⁻⁵

In this investigation efforts were concentrated on developing a procedure whereby the impure metal would be readily converted to a salt of yttrium which could be more easily purified than the metal itself.

Available thermodynamic data indicated that yttrium metal would reduce MgCl_2 to form YCl_3 and magnesium metal. This reaction appeared particularly favorable since the products, YCl_3 and magnesium, have sufficiently high vapor pressures to be purified by distillation in vacuo at 1000°C . By reacting this purified mixture with calcium metal, a Y-29 wt% Mg alloy would be obtained that could be processed to yttrium metal by the intermediate alloy process developed at the Ames Laboratory.

EXPERIMENTAL PROCEDURE AND RESULTS

Materials

For this investigation it was necessary that the yttrium metal be free only of significant amounts of surface contaminants and for the MgCl_2 to be anhydrous in order to avoid contamination from the reaction crucible. Therefore only limited purification of these materials was needed. However, more elaborate means were taken to purify the calcium metal used in the reduction step to prepare the Y-29 wt% Mg alloy.

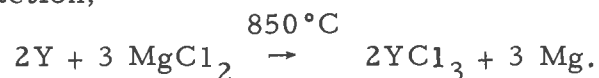
Yttrium metal of varying purity was available in the form of sponge and arc-cast ingots as well as scrap pieces of massive metal, turnings, chips, and metal fines. The turnings and chips were degreased in trichlorethylene and air dried before they were used while the sponge and ingots were used without any surface treatment. The yttrium metal fines

were excluded from this work because of the potential fire hazard involved and their high impurity content.

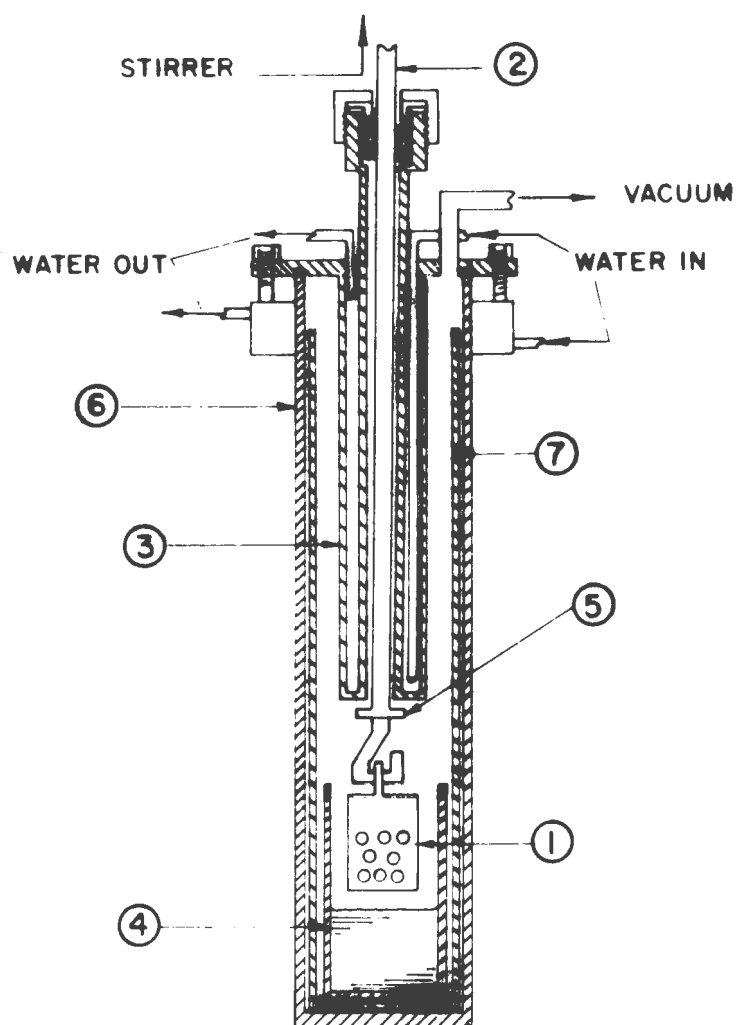
The MgCl_2 was obtained from the Dow Chemical Co. This material, which contained small amounts of water, was first dehydrated in a stream of anhydrous HCl gas at 450°C . The calcium metal that was used as the reductant for YCl_3 was obtained from the New England Lime Co. and purified by vacuum distillation at 900°C as described by Wilhelm and Carlson.⁶

Preparation and Purification of YCl_3 and Magnesium

The crude yttrium was reacted with anhydrous MgCl_2 at 850°C under a protective argon atmosphere to form YCl_3 and magnesium according to the reaction,



The YCl_3 and magnesium were then purified by co-distillation at 1000°C under a pressure of 50μ . Both the dissolution and co-distillation operations were performed in a single heating step. The apparatus employed is shown in Fig. 1. The retort (6) was 6 in. in diam and was made of 309 Cb stabilized stainless steel. The reaction crucible (4) perforated container (1) and outer crucible (7) were made of titanium sheet 0.045 in. thick. The unit was heated by an electric furnace and evacuated by a mechanical pumping system equipped with a cold trap.



1. Perforated container
2. Stirring rod
3. Water-cooled condenser
4. Ti crucible for MgCl_2
5. Tapered plug
6. Stainless steel retort
7. Ti outer crucible

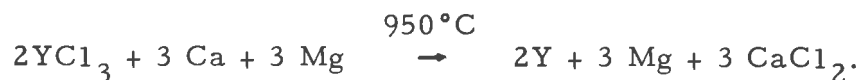
Fig. 1. Apparatus for both the dissolution of yttrium metal and the co-distillation of YCl_3 and Mg.

A typical run consisted of placing 1515 g of MgCl_2 into the titanium crucible (4) and 1000 g of crude yttrium metal into the perforated titanium container (1) which was attached to a stirring rod (2) that passed through the water-cooled condenser (3). The system was evacuated and the reaction crucible (4) heated to 600°C to allow outgassing to take place. Argon gas was then admitted to a pressure of 2 psi gauge and the temperature raised to 850°C . After the MgCl_2 had melted the container with the yttrium was lowered into the molten salt and stirred with an external motor. Although the dissolution process takes place rather quickly, the reactants were stirred 30 min to insure completion of the reaction. At the end of this time the stirring rod was raised so that the tapered plug (5) sealed the bottom of the condenser.

The pressure in the system was then lowered to $40\ \mu$ and the temperature increased to 1000°C and held for 40 h so that the YCl_3 and magnesium were co-distilled and collected on the water-cooled condenser. Since magnesium metal has a considerably higher vapor pressure than YCl_3 it distilled first and collected directly on the water-cooled condenser. The less volatile YCl_3 then deposited on the magnesium layer.

Preparation of Y-29 wt% Mg Alloy

The purified YCl_3 was reduced by calcium in the presence of magnesium to form a Y-29 wt% Mg intermediate alloy according to the reaction,



The purified calcium was placed in the bottom of a tantalum metal reduction crucible which was inserted into a stainless steel retort of the same size used in the dissolution and distillation step. The cover assembly and condenser containing the distilled YCl_3 and magnesium was then attached to the retort, and the sealed unit was outgassed by heating to 600°C under a pressure of $50\ \mu$. Argon gas was admitted to a pressure of 2 psi gauge and the retort heated to 950°C for one hour. During this step the cooling water to the condenser was turned off causing the YCl_3 and magnesium deposits to melt and drip into the tantalum crucible containing the calcium reductant.

After one hour the retort was removed from the furnace and tilted to allow the molten Y-29 wt% Mg alloy and CaCl_2 slag, which are immiscible, to solidify on the side of the tantalum crucible thus permitting easy removal.

Preparation of Yttrium Metal

The purified yttrium metal was obtained from the Y-29 wt% Mg alloy by heating the alloy in vacuo to remove the volatile components as described by Carlson et al.⁷ The resulting sponge was then arc melted in an inert atmosphere and evaluated by chemical and microscopic analysis. Typical analytical data of the arc-melted crude or scrap yttrium metal are shown in Table I. The purification of the yttrium is further illustrated in Figs. 2 and 3 which show the crude yttrium before and after processing.

Table I
Analysis of Arc-Cast Yttrium Metal
Before and After Purification

Element	Crude Yttrium (ppm)	Purified Yttrium (ppm)
C	375	140
N	230	60
F	900	30
O	2700	1300
H	100	150
Cr	125	75
Fe	180	75
Ni	500	220
Si	~ 150	< 100
Ta	< 400	< 400
Ti	1500	40

Samples of the purified yttrium were electron beam melted in an effort to obtain further refinement of the metal. By this treatment the hydrogen and chromium contents were decreased to <10 ppm and <35 ppm respectively, while the concentration of other impurities remained unchanged. A photomicrograph of the electron beam-melted yttrium is shown in Fig. 4.

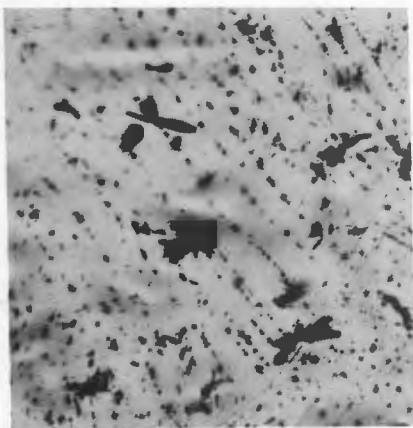


Fig. 2. Commercial yttrium as arc-cast. As electropolished in HClO_4 . 250X.

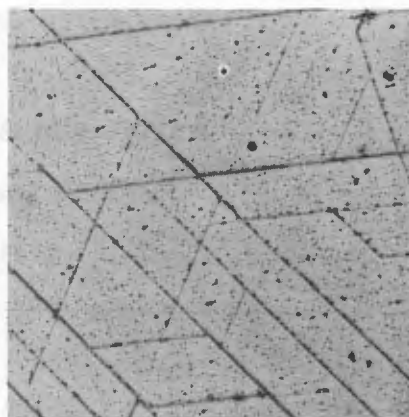


Fig. 3. Purified yttrium as arc-cast. As electropolished in HClO_4 . 250X.

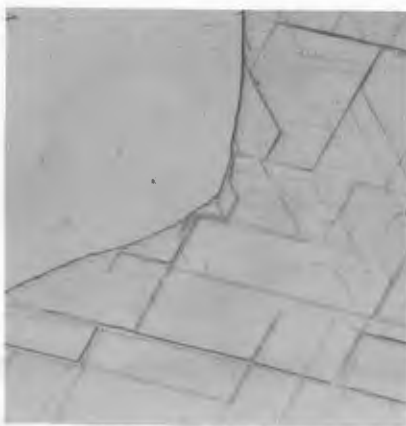


Fig. 4. Yttrium metal as electron beam melted. As electropolished in HClO_4 . 250X.

Other Procedures Used for Metal Refinement

Other procedures were considered for purifying crude yttrium metal. One of these methods was to dissolve the impure material in HCl with subsequent crystallization of $\text{YCl}_3 \cdot 6 \text{H}_2\text{O}$ from solution by evaporation. After removing the water from this hydrated compound the YCl_3 could be reduced to yttrium metal using calcium or lithium as the reductant. This method was abandoned since a considerable length of time was required to thermally decompose the $\text{YCl}_3 \cdot 6 \text{H}_2\text{O}$ to high purity YCl_3 . Another procedure involved the conversion of impure yttrium to oxide which could be purified and processed to yttrium metal by one of several methods.⁸ However, this approach was also rejected since many of the impurities present as oxides could be removed only by ion exchange processing.

It was found that the intermediate Y-29 wt% Mg alloy obtained in this work was always low in impurity content except for oxygen. The oxygen was contributed by the calcium reductant or it was entrained with the magnesium or YCl_3 during the co-distillation step. In separate experiments this impurity was decreased to 400 ppm in the yttrium metal by contacting the Y-29 wt% Mg alloy with fused YCl_3 .

A decrease in oxygen content was also accomplished by using YCl_3 as an extractant and simply adding a deficiency of calcium metal in the reduction step so that the slag consisted of $\text{CaCl}_2 - 25 \text{ wt\% } \text{YCl}_3$. In these experiments enough magnesium metal was also removed from the charge

prior to the reduction so that the resulting alloy contained 29 wt% Mg. Yttrium metal prepared in this way contained 800 to 1000 ppm oxygen.

By employing the process described in this investigation in conjunction with the various refining procedures, scrap or crude yttrium has been purified with 80-85% recoveries of metal consistently being obtained. Although this process was developed on the pound scale little difficulty should be encountered in processing several hundred pounds of yttrium per batch, since the reduction step for the preparation of the intermediate alloy has already been proven in the production of large quantities.

SUMMARY

1. A process has been developed by which commercial grade yttrium metal of 99.3 wt% purity can be upgraded to metal of 99.8 wt%.
2. By employing an additional refining step in which the Y-Mg intermediate alloy is contacted with fused YCl_3 , the oxygen content of the metal was reduced from 1300 to 400 ppm thereby producing metal of 99.9 wt% purity.
3. Yttrium having an oxygen content of 800 to 1000 ppm can be obtained if the reduction is calcium deficient so that the slag produced contains YCl_3 which is an extractant for oxygen in the Y-29 wt% Mg alloy.
4. The hydrogen and chromium contents of the purified yttrium can be lowered by electron-beam melting.
5. There is no apparent reason why this process could not be used to purify large quantities of yttrium metal.

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